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A CONTRIBUTION TO THE KNOWLEDGE OF TRIPHENYLMETHYL

BY
L. H. CONE

A THESIS SUBMITTED TO THE FACULTY OF THE DEPART-
MENT OF LITERATURE, SCIENCE, AND THE ARTS
OF THE UNIVERSITY OF MICHIGAN FOR
THE DEGREE OF DOCTOR OF
PHILOSOPHY.

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The experimental work for the following paper was done under the direction of Professor M. Gomberg in the chemical laboratory of the University of Michigan. During the entire course of the work Professor Gomberg has taken a constant and enthusiastic interest in its progress, and for this I wish to express my sincerest appreciation.

ON TRIPHENYLMETHYL

BY L. H. CONE.

In 1900 Prof. M. Gomberg discovered and isolated triphenylmethyl.¹ In attempting to prepare hexaphenylethane by the action of metals upon solutions of triphenylmethylchloride he obtained a very insoluble, crystalline, colorless compound. This substance contained oxygen, and could therefore not be hexaphenylethane. As the only substances present in the reaction mixture had been triphenylmethylchloride, oxide-free metal, and the solvent benzene, the source of the oxygen present in the final product must be the air. The action of metals upon triphenylmethylchloride in benzene solution was then tried in an atmosphere of carbon dioxide. As soon as the metal, preferably zinc, came in contact with the benzene solution of the triphenylmethylchloride, this solution began to turn yellow. The reaction was allowed to continue till the benzene solution was halogen free and the benzene was then evaporated in an oxygen free atmosphere. A solid hydrocarbon was obtained which Prof. Gomberg has named triphenylmethyl. This triphenylmethyl is powerfully unsaturated. A solution of it in any solvent when exposed to air will be decolorized in a few minutes and some of the same insoluble oxygen containing substance, obtained in the first attempt to prepare hexaphenylethane, will be formed. This oxygen containing substance has been shown to be a peroxide of triphenylmethyl. A solution of triphenylmethyl will also take up iodine very rapidly to form triphenylmethyl iodide. This strong unsaturation of triphenylmethyl led Prof. Gomberg to assume that the action of metals upon triphenylmethylchloride consists simply in the removal of the halogen, the residue $(C_6H_5)_3C$ remaining as such in solution.

The work, the results of which are given in this paper, was taken up in order to gain more evidence from the physical and chemical properties of triphenylmethyl upon which to base conclusions as to its constitution. The method of preparation of the hydrocarbon, as worked out by Prof. Gomberg, is first given, then a study of its physical properties including solubilities, melting point, molecular weight, and its electrical conductivity when dissolved in liquid sulphur dioxide. The chemical reactions studied are its oxidation to triphenylmethylperoxide, including a number of the reactions of the latter, its addition reactions

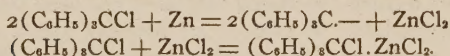
¹ Journ. Am. Chem. Soc. 22, 757 (1900).

with a large number of organic esters, ethers, ketones, hydrocarbons, etc., and finally its decomposition in benzene and carbon tetrachloride solutions under the influence of light.¹

I. PREPARATION.

On account of the strong affinity of triphenylmethyl for the oxygen of the air, special apparatus which will permit the use of an indifferent gas during the entire course of the reaction is needed for its preparation. Such an apparatus was constructed some time ago by Prof. Gomberg and has been found to answer the purpose admirably. Following is a description of the apparatus as it is used.

A (Plate I) is an ordinary Dreschel bottle, to which two three-way stop-cocks have been sealed. Twenty grams of triphenylmethylchloride are placed in this bottle, and dissolved in 100 cc. of benzene. Three or four rods of zinc, about three inches long, are placed vertically in the solution. After a rapid stream of carbon dioxide has been passed through the bottle to displace the air, the stop cocks are closed. In a short time dark viscous drops of a double salt of zinc chloride with triphenylmethylchloride will begin to gather on the rods and flow gradually to the bottom of the Drechsel. By this flowing of the double salt from the vertical rods a fresh, large surface of the zinc is continually exposed throughout the entire course of the reaction. The reaction, which begins as soon as the zinc comes in contact with the solution of triphenylmethylchloride, consists first, in the formation of triphenylmethyl, due to the withdrawal of chlorine from the triphenylmethylchloride, and second, in the formation of a heavy, viscous, double salt of zinc chloride with unused portions of triphenylmethylchloride. The reaction may be represented as follows:



It is thus evident that only two thirds of the triphenylmethylchloride employed in the reaction is changed to triphenylmethyl. After the reaction is complete, A is connected with the apparatus B, as indicated in the figure. B is then repeatedly exhausted and refilled with dry carbon dioxide, and finally, with B exhausted, the stop cocks C and b are so turned that the liquid in A is drawn over into B. A small additional portion of benzene is then drawn in through D, to A and then to B, in order to wash the zinc and the insoluble double salt free from adhering triphenylmethyl. A is then disconnected from B. A rubber tube through which steam is passing is then wound around the lower half of B, and the benzene distilled off under diminished pressure. The receiver is packed

¹These results have already been published in four papers in the *Berichte der Deutschen Chemischen Gesellschaft*: 37, 2034, 3538 (1904); 38, 1333, 2447 (1905).

in ice in order to condense the benzene. After the benzene has been completely driven off, *H* is disconnected from the receiver, about 50 cc. of hot acetone are added through the funnel *E* and the apparatus shaken vigorously till the lumps of triphenylmethyl are broken up. *B* is then filled with carbon dioxide and allowed to stand till the acetone is cold. The distilling flask *B* is connected with a suction flask by means of the rubber stopper below *G* and by slightly turning the stop cock *G* the acetone may be drawn off, leaving the crystals in the flask *B*. Fresh portions of acetone may then be added through the funnel *E* and drawn through to thoroughly wash the crystalline mass in *B*. By alternately exhausting and refilling *B* with dry carbon dioxide, the solid product may be completely dried in the course of an hour. When dry, triphenylmethyl is quite stable and may be exposed to the air for some time without appreciable oxidation. The triphenylmethyl thus obtained is very pure and can be used for most experimental purposes. The solid is removed from *B* by cutting the apparatus open at *c* while a slow stream of carbon dioxide is kept flowing.

Solubilities.:—As thus prepared triphenylmethyl is at first almost colorless; but on standing it assumes a light yellow color which gradually becomes deeper. These changes take place a great deal faster when the substance is exposed to air than when it is kept in a dry, oxygen-free atmosphere. It is almost completely insoluble in petroleum ether, monochloroacetic ester, and chlorcarbonic ester, slightly soluble in chlorbenzene and in benzylchloride, and in methyl and ethyl alcohols on warming. It is moderately soluble in carbon tetrachloride and toluene in the cold but decidedly soluble on warming. It is fairly soluble in ethyl iodide and in ethylene bromide, while in chloroform and in carbon disulphide it is very soluble both when hot and cold.

Melting Point.:—The melting point of triphenylmethyl must evidently be obtained in an atmosphere free from all oxygen. Several observations were made upon large quantities, 2 or 3 grams, but uniform results were not obtained so easily as by the following more simple method. A long melting point tube is bent in a U shape. A few millimeters of the tube are filled with triphenylmethyl while a slow stream of carbon dioxide is kept flowing through it. One end of the tube is quickly sealed off and the other end is drawn out into a very fine capillary, long enough to project from the melting point apparatus, and then sealed off. The tube is fastened to the thermometer with that portion of the tube containing the triphenylmethyl, usually the elbow, by the bulb of the thermometer. After the temperature of the bath has begun to rise steadily the projecting end of the melting point tube is snipped off. The fineness of the capillary will prevent any backward diffusion even though the rise of temperature is slow. The melting point of even the purest sample of the hydrocarbon is somewhat unsharp, extending over about two degrees,

i. e., from 145-147°. As the melting point is approached the triphenylmethyl turns dark and upon melting gives a dark red liquid.

Distillation.—It was hoped that the hydrocarbon might be stable enough to stand distillation under diminished pressure, and thus afford an additional means of purification. This has not proven to be the case under the lowest pressure obtainable by a water pump. At 19mm pressure the hydrocarbon decomposed at about 206°. A considerable quantity of triphenylmethane, along with a yellowish oil and vapor came over.

II. MOLECULAR WEIGHT.

The choice of an indifferent gas to be used in the molecular weight determinations depends upon its insolubility in the solvents to be employed. Carbon dioxide is relatively quite soluble in many organic solvents and for this reason its use is entirely barred. For example, it was found that a very short exposure of benzene to an atmosphere of this gas lowered the freezing point of the solvent as much as 0.5°. After some experiments nitrogen was selected as being the most suitable gas for the purpose.

Beckmann has lately shown that his electrical mechanical stirrer gives very satisfactory results with the freezing point method.¹ His apparatus has served admirably in determining the molecular weight of triphenylmethyl because it facilitates the exclusion of oxygen.

The freezing point apparatus was constructed as follows: In the rubber stopper carrying the Beckmann thermometer a small hole was bored at one side so that the thermometer would still remain centered in the freezing point vessel. Through this hole was passed one arm of a T tube, the other two being, one for attachment to the drying train and the other, carrying a stop cock, to the pump. The freezing vessel was carefully cleaned, the ordinary Beckmann two-ring stirrer inserted, and the stopper, carrying the thermometer and T tube, sealed in place with wax. The vessel was then placed within the ring of the magnet, and the magnet allowed to rest upon a plate of asbestos. The freezing bath was on an adjustable stand and could be raised and lowered according as it was necessary to freeze or thaw the solvent. With high boiling solvents such as nitrobenzene, the freezing vessel was exhausted and refilled with nitrogen after the solvent had been added, but with benzene the air was first replaced with nitrogen and the solvent then run in through the side arm, while a stream of nitrogen was flowing to prevent the entrance of air. The nitrogen before entering the freezing vessel was passed through alkaline pyrogallol and then carefully dried by means of sulphuric acid, soda lime, and calcium chloride.

In carrying out a determination it is necessary to maintain a con-

¹Zeitschr. für physikal. Chem. 44, 169 (1903).

stant pressure on the bulb of the thermometer or very decided variations in the height of the mercury column will result. Beckmann¹ has called attention to the influence of pressure on the bulb of the thermometer in a general way but a few observations made during the carrying out of the present piece of work show clearly how great this effect of pressure may be. It was found that an increase of pressure on the bulb of the thermometer used in this work equal to 5mm of mercury would produce a corresponding rise in the reading of the thermometer of 0.001°. If in the use of the Beckmann stirrer the freezing vessel is tightly closed at room temperature and then cooled down to the freezing point of benzene, a decrease within the vessel of as much as 25mm of mercury may result. If the vessel be then opened when still cold, as is usually done, and the substance to be experimented upon added the pressure will be nearly atmospheric at the next reading. By using this very procedure variations of as much as 0.002-0.004° were readily obtained in the freezing point of the pure solvent, when under constant pressure the freezing point did not vary appreciably. In very accurate work this is not a negligible error especially as it may be so easily avoided. When air is used as an atmosphere the only safe way is to have some method of equalizing the pressure, such as a stop cock in the side arm. When using any other atmosphere, as for example nitrogen in this work, the gasometer pressure must be kept constant during any series of readings. By observing this precaution, we obtained very satisfactory results with the Beckmann stirrer.

In all of the molecular weight determinations triphenylmethyl which had been purified by washing with acetone, was used in the form of tablets. To prepare these tablets with the minimum amount of oxidation the dry hydrocarbon was poured directly from the apparatus B, above described, into a tube of about 1cm internal diameter. A carbon dioxide generator was connected with this tube so that whenever it was opened a stream of gas passed through. Successive portions of the substance were shaken out into a pellet machine, quickly compressed, and dropped into a test tube filled with carbon dioxide. By placing the tightly stoppered test tubes in a dessicator filled with carbon dioxide, the pellets could be kept for a number of days in comparative purity.

A large variety of solvents were used in the molecular weight determinations in order to be sure that the results were not in any way influenced by the nature of the solvent. The solvents employed were: (1) benzene and naphthalene, (2) nitrobenzene, (3) dimethylaniline, (4) p-bromtoluene, and (5) phenol. The benzene and naphthalene were the purest obtainable, the benzene carefully fractionated and the naphthalene carefully resublimed. Nitrobenzene has been investigated as a solvent

¹ Zeitschr. für physikal. Chem. 44, 180 (1903).

for the cryoscopic method by G. Ampolla and Carlinfanti.¹ From their experiments they have found the constant 69.07. The nitrobenzene for our work was prepared from Kahlbaum's thiophene free benzene. It was dried and carefully fractionated three times, the final product distilling within a range of 0.4°. The dimethylaniline (Kahlbaum's) was carefully fractionated. This solvent has been used by G. Ampolla and C. Rimatori² and they have determined the constant to be 58. The p-bromtoluene was made from Kahlbaum's toluidine by the Sandmeyer reaction. It was repeatedly fractionated till the final product was colorless and crystallized homogeneously. Paterno³ has investigated this solvent and deduced the constant 82.2. The phenol was a completely anhydrous sample distilled under diminished pressure within 1°. Its constant is 72. Tests with known substances were made to determine the purity of these solvents. The molecular weight of naphthalene, when dissolved in the nitrobenzene, was found as 129, and when dissolved in the p-bromtoluene was found as 135 (calc. 129). When dissolved in the dimethylaniline the benzene gave a value of 77.4 for its molecular weight (calc. 78).

From the tabulated results of the measurements made upon triphenylmethyl given further on, it will be seen that the values obtained with some of the solvents vary considerably from the mean. This is especially true of naphthalene which gives values uniformly too low. The high temperature of the melting point of the solvent, 80°, suggests possible decomposition. Phenol was a very unsatisfactory solvent, because it required inoculation and this could be done only with difficulty under the conditions of our work. In addition some other undetermined factor caused the freezing point of that solvent to fall steadily after the first addition of triphenylmethyl. The single result given for phenol is the one obtained from the first freezing after the only addition of the hydrocarbon made. The mean result with p-bromtoluene (495.6) is a little higher than the general average. This solvent, as it freezes at about 25°, can be worked with at room temperature, thus eliminating many troublesome precautions as to constancy of the bath. Nitrobenzene, giving a mean result of 487°, and benzene that of 491.6°, were both very satisfactory to work with. One may be substituted for the other without change, either of the bath or of the thermometer setting. For some unaccountable reason the results obtained from dimethylaniline were somewhat variable. The same tendency to variation is shown in the molecular weights of a number of substances as found by Ampolla and Rimatori.⁴ The mean of the values which we have obtained for triphenylmethyl in dimethylaniline is 474.9.

¹Gazz. chim. Ital. 26, II, 76 (1896).

²Ibid. 27, I, 51 (1897).

³Ibid. 26, II, 1 (1896).

⁴Gazz. chim. Ital. 27, I, 53 (1897).

In no case was the triphenylmethyl more than two days old. With 7 samples of the hydrocarbon the preparation and the determinations were made the same day. The solutions of triphenylmethyl seldom showed more than a trace of the peroxide and then only in the more concentrated solutions. The results of the measurements are given in the following table. They are numbered in the order in which they were obtained.

TABLE OF MOLECULAR WEIGHTS.

Calc. for $(C_6H_5)_3C = 243$.

No.	SOLVENT	Age of Substance in days	Grams Solvent	Grams Dissolved Triphenylmethyl	Δ	M Found
1	Benzene	< 1	24.53	0.5994 1.1320	0.267 0.469	457.3 491.9
2	Benzene	< 1	12.36	0.3030 0.7760	0.248 0.586	490.6 532.5
3	Naphthalene	< 1	15.90	0.4931	0.519	412.1
4	Nitrobenzene	1	15.90	0.2330 0.6914	0.208 0.594	486.5 505.6
5	Dimethylaniline	< 1	12.80	0.1822 0.4204 0.6489	0.191 0.413 0.630	431.6 460.4 465.0
6	p-Bromtoluene	2	15.67	0.2665 0.4972	0.274 0.517	509.5 504.5
7	Naphthalene	2	18.30	0.4552 0.8607 1.1400	0.421 0.776 1.026	407.6 418.1 419.5
8	p-Bromtoluene	< 1	21.30	0.5102 0.9556 1.8120	0.404 0.762 1.463	487.3 484.0 478.1
9	Nitrobenzene	1	17.02	0.4902 0.8914	0.419 0.752	474.8 481.1
10	Benzene	< 1	13.10	0.3801 0.7964 1.1850	0.297 0.625 0.915	488.4 486.3 494.4
11	Dimethylaniline	< 1	11.58	0.3861 0.7040	0.385 0.682	502.3 515.4
12	Phenol	1	12.50	0.3050	0.370	474.8
Mean Value						477.

The results as given show clearly that triphenylmethyl in solution consists of some kind of a double molecule. We attempted to determine whether this doubling up is caused by the process of isolation of triphenylmethyl, or whether the hydrocarbon exists in this condition immediately upon its formation. If the latter is true, then, having determined the freezing point of the pure solvent, that of a solution of known strength of triphenylchloromethane in that solvent, and, having added some metal whose chloride is insoluble, we should expect the freezing point of the solution to rise as the triphenylmethyl is formed. When the reaction is complete the depression of the freezing point should be exactly half of

that for the solution of the chloride, provided that the dimolecular "triphenylmethyl" is the only product formed. The number of molecules in solution will be continually decreasing during the course of the reaction and finally will become only half of the original. This change in the number of the molecules may be followed by observing the corresponding change in the freezing point depression. The percentage of change can

be found at any time by the formula $X = \frac{(\Delta - \Delta') \cdot 2.100}{\Delta}$ where Δ is the

depression of the freezing point of the solvent by the triphenylmethylchloride and Δ' is the observed varying depression after the metal has been added to the solution. Nitrobenzene was chosen as the solvent and silver as the metal for testing the reaction. The effect of molecular silver was first tried upon the freezing point of the pure solvent. The effect found was so small that it seemed unnecessary to introduce any correction.

In the appended tables are given two series of experiments with nitrobenzene as the solvent. While other solvents were tried, in none of them did the reaction seem to take place as rapidly. A great many variable factors enter in, such as the surface of the silver, the rate of stirring, the temperature of the reaction, etc. We hope later, however, to take up a more thorough study of the reaction by this method.

Tables in which are shown the decrease of the freezing point depression of a triphenylmethylchloride solution as triphenylmethyl is formed.

0.4586g Triphenylmethylchloride, dissolved in 20.03g Nitrobenzene, gave $\Delta = 0.567^\circ$.

Molecular Weight of $(C_6H_5)_3CCl$: Calc. M. 278. Found M 279.

Temperature of the experiment	G of Silver present	Time in minutes	Δ'	Molecular weight found	% Change
...	...	...	0.567°	279.	0.0
22°	0.5	11	0.543	291.4	8.5
22°	0.5	66	0.507	312.	21.2
45°	0.5	116	0.469	337.3	35.3
45°	0.5	195	0.419	377.6	52.2
45°	1.0	225	0.327	483.9	84.6
45°	1.0	255	0.311	508.6	90.3

0.8161g Triphenylmethylchloride dissolved in 16.94g Nitrobenzene gave $\Delta = 1.197^\circ$.

Molecular Weight of $(C_6H_5)_3CCl$: Calc. M. 278. Found M 277.9.

Temperature of the experiment	G of Silver present	Time in minutes	Δ'	Molecular weight found	% change
...	...	...	1.197°	277.9	0.0
10°	0.7	11	1.029	323.4	28.1
13°	0.7	26	0.984	338.1	35.6
13°	0.7	70	0.889	374.2	51.5
18°	0.7	110	0.799	413.9	66.5
18°	0.7	140	0.734	453.3	77.4
50°	0.7	155	0.724	459.6	79.0
50°	1.2	190	0.642	518.3	92.7
50°	1.2	225	0.647	514.3	91.9

The figures given in column five as the experimentally observed values of the molecular weight of the mixture are calculated upon the amount of triphenylmethylchloride taken at the beginning of the experiment. Calculated upon the basis of triphenylmethyl each value would be only 87.4% of the one given. The final result for triphenylmethyl would then be, in table A: 444.5 and in Table B: 453.

The important fact brought out by all of the molecular weight tables is, that in solution, even at the time of formation triphenylmethyl has a molecular weight twice that which has ordinarily been assumed for it. Some time ago a few molecular weight determinations were made by Prof. Gomberg,¹ which gave indications of a dimolecular structure, but nothing definite enough was obtained to warrant a change of constitutional formula. The formula $(C_6H_5)_2C$ which has been used was the best expression of the facts then known. The bearing of the new fact upon the accepted view of the constitution of triphenylmethyl will be discussed further on in this paper.

III. CONDUCTIVITY.

It has previously been shown² that triphenylmethyl salts, such as the halides, are good electrolytes when dissolved in certain ionizing solvents, especially liquid sulphur dioxide. Walden³ has also shown that triphenylmethyl itself possesses considerable electrical conductivity. The sample upon which he worked was rather old, having been prepared in this laboratory and sent to him. This may perhaps account for the nonuniformity of the results which he has obtained. The conductivity of the hydrocarbon has been now measured on freshly prepared samples, carefully recrystallized from a mixture of chloroform and petroleum ether. The results which have been obtained agree among themselves within the limits of error of the experiment and prove beyond any doubt the remarkable fact that triphenylmethyl is, under these conditions, a good electrolyte.

After this work upon the conductivity of triphenylmethyl had been all completed and the results published, it was found that triphenylmethyl crystallized from petroleum ether contains a portion of the solvent held in some form of combination. (See page 24.) As the triphenylmethyl used in making these conductivity measurements had all been crystallized from a mixture of chloroform and petroleum ether it may have contained as much as 15% of combined solvent. An analysis made upon a small quantity of the crystals of triphenylmethyl which had been sealed up at the time of making the conductivity measurements showed that they contained 9% of volatile matter. A special experiment showed that the hydrocarbons from petroleum ether which combine with triphenylmethyl do not in themselves possess any conductivity when dissolved in liquid

¹ Ber. d. chem. Ges. 34, 2731 (1901).

² Walden. *ibid* 35, 2018 (1902); Gomberg *ibid* 35, 2405 (1902).

³ Zeitschr. für physik. Chem. 43, 443, (1903).

sulphur dioxide. The error produced therefore by the presence of these impurities is in such a sense that the conductivities are probably smaller by from 10-15% than they should have been for pure triphenylmethyl.

The cell used in the conductivity measurements is shown in Plate III. The electrodes, both attached to the same Y tube, are 1x1.5 cms, 0.8cms apart. Connection is made by a drop of mercury in the bottom of each arm, into which carefully insulated wires lead. The outer ends of these wires are sealed into small tubes which, filled with mercury and fastened to the electrode stem, serve as outside contacts. The electrodes were only slightly platinized. The constant of the cell was determined by a hundredth normal potassium chloride solution at 25° C.

Commercial sulphur dioxide was carefully dried by means of sulphuric acid and phosphorus pentoxide, and condensed directly in the cell. The volume of solvent was determined from its weight, according to Walden's practice.¹ All of the measurements were made at 0°. A solid rubber stopper was employed in the side arm of the cell. To hold it in place against the internal pressure, a piece of rubber tubing was wired to the side arm, and compressed about the stopper by a wire each time before the temperature was raised.

The method of procedure was as follows. A carefully recrystallized sample of triphenylmethyl was prepared, and successive small portions were sealed in tubes of about one mm. internal diameter, filled with carbon dioxide. The tubes being very light, it was possible to determine the amount of substance with a certainty to 0.1 mg. About 25 cc. of sulphur dioxide were condensed in the cell, and the volume determined by the gain in weight. The cell was then placed in a thermostat filled with fine ice and distilled water, and allowed to remain till the conductivity of the liquid became constant. After being again cooled in a freezing mixture the first addition of triphenylmethyl was made. The cell was then returned to the thermostat, and readings taken at intervals till they became constant, which usually took about fifteen minutes. The additions of the hydrocarbon were repeated under the same conditions, till the solution began to show visible signs of peroxide. The first addition, even though as small an amount as 0.8 mg., gave the solution a strong yellow color which grew deeper with successive additions.

To test the combined effects upon the conductivity of the liquid sulphur dioxide of the moisture absorbed during the various openings of the cell, as well as of the carbon dioxide poured out of the tubes with the triphenylmethyl, a blank experiment was carried out. This experiment was performed under exactly the same conditions as were involved in the actual measurements, except, that no triphenylmethyl was added. Five successive openings of the cell were made at intervals of an hour and it was found that the specific conductivity of the sulphur dioxide was

¹ Zeitschr. f. physik. Chem. 39, 518.

thus raised from 0.4×10^{-6} to only 0.7×10^{-6} , an error much smaller than many others involved in the actual measurements.

The results as obtained are given in the following table. Each set of measurements was made upon an entirely fresh sample of triphenylmethyl sealed up as soon as prepared.

Conductivity of Triphenylmethyl in Liquid Sulphur Dioxide
at 0° . $M = 486$.
(4 Different Sets of Measurements.)

I		II		III		IV	
V	μ	V	μ	V	μ	V	μ
4276	69.19			2376*	65.9	14840	78
922	65.00	1038	81.7			6956	84.5
460	62.5	484	63.0			2342	82.0
330	57.8	320	51.3	274*	44	1416	73.0
274	53.6	246	49.4	140	29.8	924	67.5
197	44.3			105.4	24.1	420	51.1
132	34.3	133	30.1	72.2	17.4	217	32.0
84	23.9	90.8	22.8	57.4	14.8		
48	16.5	47.5	14.4	40.	10.2		

V = Volume in liters containing 1 gram-molecule of solute.

μ = Molecular conductivity.

The results of the measurements are best shown in the accompanying curves (Plate II). They are plotted from the results calculated upon a basis of 486 as the molecular weight of triphenylmethyl. That the curves do not coincide at high dilutions is not strange. The many sources of error inherent in the method render exact determinations, such as are made for the inorganic salts, well nigh impossible. The molecular conductivity of the hydrocarbon increases regularly with the dilution, similarly to inorganic electrolytes, and reaches a maximum value at about 80, when the dilution is above 2,000 liters.

IV. FORMATION AND REACTIONS OF TRIPHENYLMETHYL-PEROXIDE.

I. FORMATION OF THE PEROXIDE.

It has been shown¹ that the oxidation of triphenylmethyl by atmospheric oxygen results in the formation of triphenylmethylperoxide, the reaction presumably taking place as follows:



There are two methods by which this reaction may be studied, the determination of the amount of oxygen absorbed by a known weight of triphenylmethyl, and by weighing the peroxide formed by exposing a known amount of triphenylmethyl in solution to the action of oxygen. Both methods have been employed.

¹ Ber. d. chem. Ges. 33, 3154 (1900).

Absorption of Oxygen by Triphenylmethyl.—To measure the absorption of oxygen by triphenylmethyl an apparatus similar to that used by Engler and Wild¹ has been employed. Freshly prepared samples of triphenylmethyl were weighed out in an atmosphere of carbon dioxide in thin walled test tubes. Since carbon dioxide is very soluble in the solvents employed the tubes were evacuated and filled with nitrogen, then with the desired solvent, and finally sealed. The displacement of carbon dioxide by nitrogen was found necessary because any dissolved carbon dioxide, on account of its partial pressure, would lead to errors in the measurements of the absorbed oxygen. The tubes were then placed in a 250 cc absorption flask containing 50-60 cc of the respective solvent. This absorption flask was immersed in a large tank of water which was kept at room temperature and was connected by thick walled rubber tubing with a water jacketed gas burette in which mercury was used as the displacing liquid. The apparatus was then filled with oxygen and the tube containing the triphenylmethyl was broken by shaking the absorption flask. Absorption of oxygen began at once and was usually complete in less than two minutes. Benzene, toluene and nitrobenzene were employed as solvents. Toluene was most satisfactory owing to its low vapor pressure and to its stability towards oxidizing agents. Nitrobenzene gave results uniformly too high, owing probably to some action of oxygen upon it. Blank experiments showed that amounts of nitrobenzene equal to those which were used in the actual experiments would take up from 1-2 cc of oxygen. Results of the experiments are given in the appended table (A). The values for the vapor pressure of benzene were taken from tables prepared by Young² and the tension of toluene was determined by ourselves.

As is apparent from the table different samples of triphenylmethyl varied somewhat in their power to absorb oxygen, but the determinations made on any one product agree well among themselves. Considering the ease with which the peroxide is likely to be formed during the preparation of the hydrocarbon, as well as the effect of sunlight upon the latter, the results seem to warrant the interpretation that the oxidation of triphenylmethyl by molecular oxygen is quantitative according to the equation given above for the formation of the peroxide, at least in so far as the amount of the absorbed oxygen is concerned.

Weighing of the Peroxide. When the peroxide formed by the oxidation of triphenylmethyl is collected and weighed the quantity is always found to be less than that required by the theory. The table below (B) contains the results of experiments carried out under two different sets of conditions. The first series were obtained by allowing the solutions, after the measurement of the absorption of oxygen as given in the previous

¹ Ber. d. chem. Ges. 30, 1673 (1897).

² Journ. Chem. Soc. 55, 501 (1889).

TABLE A.

Absorption of Oxygen by Triphenylmethyl.

(The theoretical value, calculated according to the equation on page 13=6.59%)

SOLVENT	Triphenyl- methyl	Oxygen absorbed	Tempera- ture	Baro- meter	Vapor ten- sion of solvent	Oxygen absorbed	Oxygen absorbed during first minute
	g	ccm		mm	mm	pCt.	ccm
Benzene	0.753	43.2	19°	736	72	6.74	..
	0.851	46.4	19	736	72	6.40	..
	0.804	43.4	20	737	75	6.46	..
	0.758	41.8	20	737	75	6.57	..
	1.131	63.8	19	730	72	6.55	41
	1.040	58.2	20	730	75	6.45	..
	0.968	53.0	19	730	72	6.36	32
	0.978	53.0	19	735	72	6.34	33
	1.094	59.2	19	735	72	6.33	41
	1.198	63.6	18	739	69	6.30	46
	1.536	81.8	18	739	69	6.32	..
	1.077	54.8	19	741	14	6.52	..
	1.035	53.7	19	741	14	6.65	..
	1.817	93.0	21	741	14	6.50	64
Toluene	1.182	60.4	21	737	14	6.48	52
	1.254	64.8	21	737	14	6.55	53
	0.785	39.3	20	736	14	6.37	..
	1.071	59.2	20	743	..	7.39	..
	1.233	66.2	20	729	..	7.05	..
Nitrobenzene	1.120	60.4	20	729	..	6.93	..
	1.007	55.0	21	734	..	7.03	..
	1.715	91.2	21	734	..	6.84	..

table, to evaporate spontaneously, and weighing the residue after washing it with ether in which the peroxide is insoluble while the oily products are very soluble. The second series was obtained by merely exposing solutions of the hydrocarbon to air and, after oxidation was complete, proceeding as above.

TABLE B.

Peroxide obtained by the action of pure oxygen upon triphenylmethyl			Peroxide obtained by oxidation of triphenylmethyl by atmospheric oxygen		
Triphenyl- methyl in g.	Peroxide in g.	Peroxide in %	Triphenyl- methyl in g.	Peroxide in g.	Peroxide in %
1.817	1.230	63.5	0.975	0.865	83.7
1.254	0.835	63.0	0.818	0.750	86.4
0.785	0.520	65.8	0.828	0.760	86.6
1.218	0.893	68.8	0.956	0.829	81.3
1.031	0.728	66.5	1.086	0.930	80.3
0.936	0.693	69.5			
1.274	1.000	69.0			

As is seen from the above results the peroxide, as determined by

weighing, is formed to the extent of only about 85% of the theory while the actual absorption of oxygen is very nearly that indicated by a quantitative formation of the peroxide. According to Engler,¹ peroxides are the first products formed in the autoxidation by atmospheric oxygen and these then may undergo internal oxidation either at once or at a slightly elevated temperature, as is the case for instance, with pinene. It is probable that this also happens in the case of triphenylmethyl, and about 20% of the peroxide in its nascent state is thus decomposed, giving rise to oily products soluble in ether. We have made no examination of this oil further than to determine that it contains about the same amount of oxygen as the peroxide itself.

2. REACTIONS OF THE PEROXIDE.

Reaction with Sulphuric Acid. When triphenylmethylperoxide is treated with concentrated sulphuric acid an intensely colored solution is obtained. This solution probably owes its color to the presence of triphenylmethylsulphate formed according to the following equation,



The oxygen which is produced according to this equation oxidizes a portion of the triphenylmethylsulphate and this accounts for the yield of only about 80% of carbinol that can be obtained by adding water to the sulphuric acid solution. Although it was not possible to isolate the sulphate directly from this sulphuric acid solution, it was obtained from triphenylmethylchloride and silver sulphate. Liquid sulphur dioxide was employed as the solvent for carrying out this reaction because of the very slight solubility of the triphenylmethylsulphate produced in organic solvents. The sulphate as thus prepared is a dark red substance forming intensely red solutions which rapidly decolorize in moist air, but are perfectly stable in dry air. When the solutions are decolorized by moisture the products of hydrolysis are triphenylcarbinol and sulphuric acid.

Analysis of the sulphate gave the following results:

0.2292 G Sbst. gave 0.1001 G BaSO₄

$[(\text{C}_6\text{H}_5)_3\text{C}]_2\text{SO}_4$ Calculated SO₄. 16.51 Found 17.97.

The too high results were caused by the presence of traces of sulphur dioxide which could not be entirely removed. The salt-like nature of the compound is demonstrated by its large conductivity when dissolved in liquid sulphur dioxide, $\mu_{10} = 49$.

Reactions of the Peroxide with Halogens. When triphenylmethylperoxide is suspended in chloroform and treated with an excess of bromine, a violent reaction suddenly takes place with evolution of heat, and

¹ Ber. d. chem. Ges. 31, 3052 (1898).

a dark-red crystalline body soon separates out. This is triphenylbromomethane pentabromide.¹ It is very unstable, the "perbromine" being given off readily, and can be titrated with sodium thiosulphate in presence of potassium iodide.

$C_{10}H_{18}BrBr_5$ Calculated Br, 55.32 Found 56.62.

When to the peroxide suspended in carbontetrachloride only the calculated quantity of bromine (1 mol. wt.) is added and the solution heated on the water bath, the peroxide soon goes into solution forming triphenylmethylbromide. By suspending the peroxide in a chloroform solution of iodine and adding bromine, products of varying composition may be obtained. In presence of a large excess of iodine triphenylbromomethane pentaiodide is formed.

With chlorine no reaction takes place unless a halogen carrier is present. 18 grams of peroxide and 1 gram of iodine were heated in boiling carbontetrachloride for three hours, while a stream of chlorine was passed through the liquid. After evaporation of the solvent an oily mass remained in which crystals of triphenylmethylchloride soon began to form. 7 grams of the chloride were obtained corresponding to a yield of 40%.

Reaction with Phosphorus Pentachloride. When triphenylmethylperoxide is heated with phosphoruspentachloride there is no reaction till a temperature of 100° is reached, when the peroxide changes into an oil with formation of large quantities of hydrochloric acid, but without evolution of oxygen. The first step in the reaction probably consists in the formation of triphenylmethylchloride and free oxygen. The oxygen then in turn oxidizes some of the triphenylmethylchloride to benzophenone which is immediately changed into the dichloride by the phosphorus pentachloride present. The hydrochloric acid must be produced by substituting action of the phosphorus pentachloride upon some of the products. That benzophenone dichloride and triphenylmethylchloride are the main final products of the reaction seems to substantiate the above explanation. Besides these two products there is always formed a small amount of diphenylenephenylmethane. This is produced by the heating of triphenylmethylchloride with phosphorusoxychloride, as was proven in a blank experiment. In the residue remaining after the removal of the above products there was always present some highly chlorinated products which were not identified. It is during the formation of these that the hydrochloric acid is probably produced.

¹ Ber. d. chem. Ges. 35, 1831 (1902).

V. COMPOUNDS OF TRIPHENYLMETHYL WITH ORGANIC SOLVENTS.

In a previous paper¹ it was shown that triphenylmethyl combines with certain esters of acetic acid to form crystalline compounds. The constant molecular ratio in which the esters and the triphenylmethyl combined, as well as the comparative stability of the compounds when once formed, led to the assumption that in these compounds one of the oxygen atoms of the carboxyl groups had become tetravalent. A further study of this reaction has been taken up in order to determine whether the formation of compounds with triphenylmethyl takes place in general with the esters of other acids. Experiments have been made upon a large number of esters and the results obtained are given below. We have found in addition, that triphenylmethyl combines with ketones, ethers, nitriles, with aromatic, and also with unsaturated aliphatic hydrocarbons, and even under certain conditions with carbon disulphide and with some constituent of petroleum ether itself.

I. COMPOUNDS OF TRIPHENYLMETHYL WITH ESTERS.

The reaction of triphenylmethyl with esters has been studied upon a series of esters of formic, acetic, propionic, butyric and valeric acids, upon esters of dibasic acids, and also upon a few aromatic esters. Triphenylmethyl was prepared as previously described. After the benzene had been evaporated from the triphenylmethyl, in the apparatus B, described above, the warm ester was added in sufficient quantity to give a clear solution. The bulb containing the solution was then set aside in a cool place, carefully protected from light. In a number of cases petroleum ether was added to hasten crystallization. After crystallization was complete the mother liquor was removed by suction and the product washed with the same ester which had been used as a solvent, except in those cases where the ester boiled above 80° when volatile petroleum ether, instead of the esters, was used for washing. The crystals were then dried by exhausting the apparatus in which they were contained, and allowing a slow stream of dry carbon dioxide to pass over them, as described in the preparation of pure triphenylmethyl. Most of the compounds thus obtained were analyzed by heating weighed quantities (1-3g.) in a stream of carbon dioxide at temperatures from 80-120°, depending upon the boiling points of the combined esters. This gave the loss of weight due to the volatilization of the esters, and as these were driven off they were condensed and saved for identification. An indirect method of analysis was employed for the compounds of those esters which boiled above 130-140°, owing to the fact that triphenylmethyl gradually decomposes at that temperature with the formation of triphenylmethane, which at that tempera-

¹ Ber. d. chem. Ges., 34, 2729 (1901).

ture is appreciably volatile. This indirect method consisted in weighing the peroxide formed from known quantities of the ester compounds. Numerous experiments upon the oxidation of pure triphenylmethyl and also upon its compounds with the more volatile esters, have shown that the yield of peroxide, while not strictly a constant, seldom varies far from 85-86% of the theoretical. (See table, page 23.) From the amount of the peroxide, then, the percentage of triphenylmethyl and ester in the original compound may be roughly calculated by use of the factor 85.5%.

After the work had been finished upon the complete series of esters and aromatic hydrocarbons, it was found that under the conditions of our experiments triphenylmethyl might give compounds with petroleum ether. Inasmuch as warm petroleum ether had been used to facilitate crystallization from many of the ester and hydrocarbon solutions, this discovery necessitated a complete revision of the work. The conditions under which triphenylmethyl does not combine with petroleum ether were first determined, and then, under these new conditions all the experiments in which petroleum ether had been used in the original work were repeated. The results as obtained are given in the table below. For the sake of brevity only one analysis is given for each ester compound although duplicates were always made both in preparation and analysis.

Ester combined with Triphenyl methyl	Compound of Ester and Tri- phenylmethyl taken in gms.	Loss in weight due to volatiliza- tion of ester in gms.	Loss in weight or ester driven off in percent	Percent ester calc. for $[(C_6H_5)_3C]_2 + 1 \text{ mol. ester}$
Methyl Formate	1.653	0.000	00.0	11.00
Ethyl Formate	2.445	0.002	00.0	13.45
Propyl	2.565	0.343	13.4	15.33
Isobutyl	2.610	0.454	17.4	17.35
Amyl	1.356	0.240	17.7	19.27
Methyl Acetate	1.438	0.186	12.9	13.45
Ethyl Acetate	1.547	0.228	14.8	15.33
Propyl	2.828	0.438	15.5	17.35
Methyl Propionate	2.455	0.366	14.9	15.33
Ethyl	1.856	0.336	18.0	17.35
Propyl	2.342	0.369	15.7	19.27
Amyl	1.385	0.213	15.4	22.90
Methyl Butyrate	1.845	0.312	16.9	17.39
Ethyl	1.561	0.231	14.8	19.27
Methyl Valerate	2.637	0.515	19.5	19.27
Ethyl Carbonate	2.142	0.329	15.4	19.04
		Peroxide found in gms.	Percent Ester cal- culated from peroxide	Calculated for $[(C_6H_5)_3C]_2 +$ 1 mol. ester $\frac{1}{2}$ mol. ester
Ethyl Oxalate	2.077	1.700	9.4	23.1 13.06
Methyl Malonate	1.525	1.106	19.65	21.36 11.90
Ethyl Succinate	2.495	1.720	23.6	26.36 15.18
Ethyl Benzoate	0.644	0.457	21.45	23.6 13.36

From the results in the table it is apparent that the combination of triphenylmethyl with esters is a very general reaction. Methyl and ethyl formate were the only two esters of all those examined with which combination did not take place. Two reasons may be assigned for the apparent anomaly of these two esters. First, the exceptional character of formic acid, with only one hydrogen atom attached to the carboxyl, makes itself felt in these lower esters, while its peculiar nature is masked by the heavier alkyl groups above ethyl. Second, the dissociation points of the triphenylmethyl compounds of these two esters may lie below the room temperature. The dissociation temperatures of the ester compounds are in general low, depending upon the boiling points of the esters. This fact was apparent in the preparation of a number of the compounds, for if crystallization began while the solution was still warm (50-70°) a very low percentage of combined ester was found, and in some cases even pure triphenylmethyl separated out. When however crystallization from solutions of these same esters did not begin till they had cooled to room temperature, the percentage of ester found in the compounds agreed nearly with the theoretical. The compounds when once obtained in the dry state are stable at ordinary temperatures and give up their combined ester very slowly even in a vacuum. In an indifferent atmosphere they may be preserved indefinitely.

The compounds of triphenylmethyl with the more volatile esters are clearly shown by the table to consist of one molecule $[(C_6H_5)_3C]_2$ in combination with one molecule of ester. The experimental conditions under which the compounds of the higher boiling esters were prepared were such that the results were not so reliable, for the reason that the washing of the products with petroleum ether to remove the non-volatile solvents also removed more or less combined ester from the surface layers of the crystals. The results for these esters are therefore lower than the theory demands. The oxidation method of analysis was used for the compounds with the esters of dibasic acids. The results show qualitatively that only one carboxyl group is involved in the reaction. As only the esters of the lower dibasic acids, in which the carboxyl groups are close together, were used, such a result is not surprising. Baeyer and Villiger found in their work upon oxonium salts¹ that such esters of dibasic acids as those used in our work take up only one molecule of acid when they form salts, thus involving only one carboxyl group.

2. COMPOUNDS OF TRIPHENYLMETHYL WITH KETONES.

It has been shown that pure triphenylmethyl can be obtained by recrystallization from either acetone or from methyl or ethyl formates. We now find that acetone is an exception in this respect among the ketones just as the formates of ethyl and methyl are among the esters. All other

¹ Ber. d. chem. Ges. 34, 2692 (1901).

ketones examined enter into combination with triphenylmethyl. Even methylethyl ketone, the next higher homologue of acetone, combines with triphenylmethyl very readily.

All of the compounds with ketones were prepared by dissolving the triphenylmethyl in the pure warm ketone and allowing this solution to stand in a cool, dark place till crystallization was complete. The presence of all foreign solvents such as petroleum ether, carbon disulphide, etc., was completely avoided, except that in the final washing of the crystalline products petroleum ether was sometimes used. There can therefore be no question as to what solvent was in combination with the triphenylmethyl. The results obtained with various ketones are given in the following table:

Ketone from which Triphenylmethyl was recrystallized	Compound of Triphenylmethyl + Ketone taken in g.	Loss in weight on heating to 110-130°	Combined Ketone in g. in %	Combined Ketone calc. for $[(C_6H_5)_3C]_2 + 1$ mol. Ketone
Acetone	2.345	0.004	00.17	10.66
Methyl-ethyl ketone	1.908	0.210	11.01	12.90
Di-ethyl ketone	2.609	0.382	14.64	15.03
Methyl-propyl ketone	2.312	0.345	14.92	15.03
Methyl-butyl ketone	2.824	0.463	16.43	17.09
Di-propyl ketone	1.328	0.212	15.96	19.00
Acetyl acetone	1.304	0.206	15.83	17.06
		Peroxide Ketone obtained	calculated	
		in g	from Peroxide	
Methyl-hexyl	3.443	2.675	13.97	20.84
Acetophenone	2.569	1.769	23.50	19.80

From the table it is apparent that the combination of ketones with triphenylmethyl is, with the exception of acetone, a very general reaction. The molecular ratio of the triphenylmethyl and ketone in all the compounds is that given by the empirical formula $[(C_6H_5)_3C]_2 + 1$ Molecule Ketone. The per cent of combined solvent obtained for some of the compounds with the highest boiling ketones falls somewhat below the theoretical, probably because the washing with volatile petroleum ether necessary to remove adhering solvent from the surface of the crystals also removed some of the combined ketone.

3. COMPOUNDS OF TRIPHENYLMETHYL WITH ETHERS.

In a previous paper¹ several compounds of triphenylmethyl with ethers were mentioned. Since then the behavior of triphenylmethyl toward a much larger number of ethers has been investigated and it has been found that the same generality of combination exists in this case as in the case of the other oxygen containing solvents. The results as obtained are given in the table below.

¹ Journ. Am. Chem. Soc. 24, 601 (1902).

Ethers from which Triphenylmethyl was recrystallized	Compound of Triphenylmethyl + Ether taken in g.	Loss in weight on heating to 110-130° or combined Ether in g. in %		Combined Ether cal- culated for [(C ₆ H ₅) ₃ C] ₂ + 1 mol. Ether
Diethyl	0.943	0.109	11.56	13.22
Methyl-propyl	2.367	0.316	13.36	13.22
Ethyl-propyl	2.133	0.319	14.96	15.33
Di-propyl	2.617	0.215	8.21	17.41
Methylal	2.130	0.292	13.70	11.00
		In vacuum		
Phenetol	1.133	0.223	19.68	20.06
Anisol	1.197	0.178	14.87	18.18
		Peroxide Ether obtained calculated in g from Peroxide in %		
Benzyl-ethyl	1.769	1.253	21.54	21.90
Phenetol	1.396	1.073	18.76	20.06
Anisol	1.771	1.382	13.55	18.18
o-Methyl cresol	2.190	1.496	24.34	20.06

All of the compounds of triphenylmethyl with ethers, except dipropyl, contain ether and triphenylmethyl in the same molecular ratio as has been observed for the ester and ketone compounds, i. e., that given by the formula [(C₆H₅)₃C]₂ + 1 Molecule Ether. For some unaccountable reason dipropyl ether did not give constant results, the ether content being low, in one sample only 2%. The crystalline product obtained was probably a mixture of pure triphenylmethyl with some of the propyl ether-compound.

The behavior of aldehydes toward triphenylmethyl still remains to be examined. One experiment has been made in which triphenylmethyl was recrystallized from iso-butyl aldehyde. The product obtained lost only slightly in weight on heating, and on oxidation gave an amount of peroxide which indicated that triphenylmethyl did not combine with this particular aldehyde. The possibility of obtaining triphenylmethyl-aldehyde compounds will, however, be further investigated as soon as possible.

4. COMPOUNDS OF TRIPHENYLMETHYL WITH NITRILES.

Only three representatives of this class have been studied, i. e., propio-, aceto-, and benzo-nitrile. With the aceto-nitrile no compound could be obtained, owing probably to the very slight solubility of triphenylmethyl in this solvent when cold which prevented obtaining a solution of any great concentration below the point of dissociation of the compound. In order to increase the solubility a mixture of chloroform and aceto-nitrile was used as solvent but the crystalline compound obtained contained only about 1% of volatile matter. With propio- and benzo-nitriles compounds of triphenylmethyl can be obtained with great ease. Triphenylmethyl is fairly soluble in propio-nitrile and the solution on standing in a cool place deposits clear colorless crystals.

1.908 g. Subst. heated to 120° lost 0.205 g.
Combined propio-nitrile

Found 10.74%. Calc. for $[(C_6H_5)_3C]_2 + 1$ Mol. Nitrile 10.16%.
Although triphenylmethyl is less soluble in benzo- than in propio-nitrile, solutions in the former solvent can be easily obtained from which crystals do not begin to separate till the solutions have cooled to room temperature. Of all the addition compounds of triphenylmethyl which have been prepared the benzo-nitrile is by far the most colorless. From a concentrated solution the compound separates out in fine snow white needles which, after drying, will, in an inert atmosphere, remain almost colorless for an indefinite period.

(1) 1.657 g. Subst. heated to 115° in a vacuum lost 0.152 g. in weight.

(2) 1.235 g. Subst. gave 1.000 g. peroxide.

Combined benzo-nitrile Found

(1) 9.17%

(2) 10.28%

Calculated for $[(C_6H_5)_3C]_2 +$
1 Mol. Nitrile 17.83%.

Calculated for $2[(C_6H_5)_3C]_2 +$
1 Mol. Nitrile 9.58%.

These analyses indicate that the compound formed with benzo-nitrile contains two molecules of triphenylmethyl to one of the nitrile. Whether in these compounds one of the molecules of triphenylmethyl is attached to the benzene ring in a manner similar to that in the triphenylmethyl-aromatic-hydrocarbon compounds, and the other one to the nitrogen is a matter of conjecture.

5. COMPOUNDS OF TRIPHENYLMETHYL WITH AROMATIC HYDROCARBONS.

A compound of triphenylmethyl with benzene has already been noticed in a previous paper. The tendency of triphenylmethyl to combine with aromatic hydrocarbons is a general one, and compounds similar to that with benzene have been prepared with toluene, ethyl benzene, and with the xylenes. The methods of preparing and analyzing these compounds were identical with those employed in the work with the esters.

Hydrocarbon combined with Triphenylmethyl	Compound Hydrocarbon+ Triphenylmeth- yl taken in gms.	Loss in weight in gms.	Volatile Hydrocar- bon found in percent	Percent Hydrocar- bon calc. for $[(C_6H_5)_3C]_2 +$ 1 mol. hc	Yield of Peroxide after correction for hydrocarbon content calc. 100 %
Benzene	1.100	0.144	13.1	13.8	84.7
Toluene	1.749	0.276	15.8	15.9	86.7
Ethylbenzene	1.316	0.229	17.4	18.0	84.7
m-Xylene	2.039	0.360	17.7	18.0	86.4
o-Xylene	1.888	0.276	14.6	18.0	88.2
p-Xylene	1.405	0.180	12.8	18.0	86.3

It is seen from the table that these compounds are composed of triphenylmethyl plus hydrocarbon in a molecular ratio similar to that of the constituents of the triphenylmethyl-ester compounds. Their empirical formulæ may therefore be written $[(C_6H_5)_3C]_2 + 1$ mol. hydrocarbon. There is a great difference between the behavior of these hydrocarbon compounds and that of the crystalline body, triphenylmethane + benzene. In a vacuum the benzene of crystallization may be rapidly removed from

triphenylmethane, while the loss in weight of the benzene compound of triphenylmethyl, when similarly treated, is very slow. Again, the generality of the combination of triphenylmethyl with so many different aromatic hydrocarbons makes it probable that the phenomenon is in some way connected with the peculiar structure of the benzene ring. The facts now known do not warrant the assigning of any constitution to these compounds, at least not until a further study has been made of the behavior of triphenylmethyl with other hydrocarbons, saturated and unsaturated.

6. COMPOUNDS WITH UNSATURATED ALIPHATIC HYDROCARBONS.

The only member of this class of solvents which was at hand in sufficient quantity for experiments was amylene. Its behavior toward triphenylmethyl is entirely analogous to that of the aromatic hydrocarbons. A number of samples of its compound with triphenylmethyl were prepared by dissolving triphenylmethyl in very pure carbon disulphide and when the solution had cooled, adding an excess of amylene. The compound soon begins to separate out in a most beautiful crystalline form, in spite of the presence of carbon disulphide.

	Loss	Found
1.155 g. Sbst. lost on heating to 100°, 0.141 g.		12.21%
0.863 g. Sbst. lost on heating to 100°, 0.105 g.		12.17
Loss Calculated for $[(C_6H_5)_3C]_2 + 1$ mol. amylene	12.6	%.

The iodine numbers of the amylene used for dissolving the triphenylmethyl and also of the distillate obtained from one of the analyses were taken, and found to be of the same order of magnitude. The solid residue left in the boat after the amylene had been driven off by heating, gave peroxide on exposing its benzene solution to air. A sample (3.716g) of amylene compound, which contained 9.54% of amylene when first prepared was placed in a small dessicator over sulphuric acid and paraffine, the air having been displaced by carbon dioxide. During five days standing with frequent exhaustions and refillings of the dessicator with carbon dioxide the sample lost 0.032g. 1.892g of this was then heated to 100° and lost 0.151g or 8%. A sample of the same compound, when first prepared, gave a perfectly normal amount of peroxide (87.3%) after correction for the amylene content, thus showing that in spite of the stability of the combination a condensation in which full carbon valences have been saturated has not taken place.

7. COMPOUNDS OF TRIPHENYLMETHYL WITH PETROLEUM ETHER.

In the discussion of the petroleum ether compounds of triphenylmethyl the following abbreviations will be used: P. E. for petroleum ether, K. P. E. for Kahlbaum's petroleum ether, and A. P. E. for American petroleum ether.

While attempting to prepare a compound of triphenylmethyl with naphthalene by bringing them together in a P. E. solution, it was found that the triphenylmethyl combined, instead of with the naphthalene, with

some constituent of the P. E. The action of P. E. alone upon triphenylmethyl was then tried. As ordinary K. P. E. (75-90°) had been used in the first experiment, benzene free P. E. from the same firm was next tried,—but with similar results. Samples of A. P. E. and K. P. E. were then carefully purified. Aromatic hydrocarbons were removed by shaking with frequently renewed nitrating mixtures for ten hours. The unsaturated hydrocarbons were then removed by shaking with a strong, alkaline permanganate solution for four or five hours. After drying and boiling with sodium the P. E.'s were distilled over sodium. The portions of these purified P. E.'s boiling from 80-90° were used for dissolving the triphenylmethyl. Owing to the slight solubility of triphenylmethyl in P. E., large quantities of the solvent (50 cc. for 6-7g) had to be used, and even then it was necessary to heat the mixture to boiling in order to obtain a clear solution. On cooling, the solution deposited clear crystals, which contained in general about 15% of P. E. The conditions necessary for the formation of these compounds were next investigated. It was found that when triphenylmethyl is dissolved in a few cc. of pure carbon disulphide and to this solution, when cold, is added P. E. at room temperature pure triphenylmethyl crystallizes out. It was further found that carbon disulphide in itself does not prevent the formation of the triphenylmethyl—P. E. compounds,—for when carbon disulphide is added to a previously heated and warm P. E. solution of triphenylmethyl, the crystals obtained on cooling contain combined P. E. It seems, therefore, reasonable to conclude that the formation of these compounds is in some way connected with the heating of the P. E. solution. A number of samples of the triphenylmethyl-P. E. compounds were then prepared from solutions in different P. E.'s and after drying thoroughly in a vacuum were analyzed.

P. E. used as solvent	Triphenylmethyl+P. E. compound taken in gms	Loss in weight at 90 110° in gms.	Loss found in percent	Loss calc. for C_6H_{10} in percent
K. P. E. Ordinary	1.533	0.220	14.35	
K. P. E. Benzene Free	2.391	0.334	13.96	
K. P. E. Purified	8.137	1.191	14.63	14.14
A. P. E. Purified	4.974	0.728	14.63	
A. P. E. Purified	2.316	0.259	11.20	

It seems very improbable that such a large constant percentage of P. E. as is shown by the table could have been mechanically occluded by the crystals of triphenylmethyl. Other substances, as triphenylchlormethane and triphenyl carbinol, were recrystallized from the same P. E. as used for the above work, but every trace of the solvent could be removed from the unbroken crystals by drying in a vacuum ten to fifteen minutes. The triphenylmethyl-P. E. compounds, on the other hand, even when finely pulverized, give up their P. E. but slowly in a vacuum, as the following experiments show. 3.513g of finely pulverized compound, which contained

11.2% of P. E. lost in vacuum over sulphuric acid and paraffine in one hour 0.007g. 1.912g of the same compound, pulverized in an agate mortar, lost during twenty-four hours in vacuum 0.037g.

The distillates from a number of analyses of the compound obtained from K. P. E. were saved, and 2-3g of the liquid were collected. An attempt was made to fractionate this liquid, but the boiling point rose steadily from 70-90°. A determination of its average boiling point by the Schleiermacher static method¹ gave 75°. Vapor density determinations were then made by the Bleier-Kohn method upon the liquid redistilled above and also upon a number of distillates from other separate analyses.

K. P. E. mol. wt. found 89.6, 89.4; Calc. for C_8H_{10} =82, C_7H_{12} =96.

A. P. E. mol. wt. found 92.5; Calc. for C_8H_{12} =84, C_7H_{14} =98.

A number of combustions made upon the same distillates as the vapor density determinations gave the following results:

P.E. from which Tri-phenylmethyl had been crystallized	Substance in gms.	C O ₂ in gms.	H ₂ O in gms.	C found in percent	H found in percent
K. P. E. Ordinary	0.1866	0.5974	0.2108	87.30	12.54
K. P. E. Purified	0.1320	0.4227	0.1460	87.34	12.28
A. P. E. Purified	0.1845	0.5808	0.2353	85.86	14.13
A. P. E. Purified	0.0917	0.2892	0.1166	86.04	14.07
Calc. for C_7H_{12}			C 87.50, H 12.50.		
			C_8H_{12} (n>5 and <10) C 85.70, H 14.30.		

What is the nature and origin of these substances?

From the analyses it is apparent that the liquid from K. P. E. must consist of hydrocarbons belonging to the series C_nH_{2n-2} , and that from A. P. E. to the series C_nH_{2n} . Both distillates decolorize permanganate solution to some extent, but add neither bromine nor iodine, and cannot, therefore, belong to the olefine or acetylene series. Whether these compounds are of cyclic nature, one ring in the hydrocarbon from A. P. E. and two in those from K. P. E. is impossible to say at present.

As to the origin of the substances three hypotheses suggest themselves. First, it will be shown in this paper that triphenylmethyl, under the influence of *sunlight*, may act as an oxidizer and decompose benzene, itself being largely reduced to triphenylmethane. It therefore suggests itself, that under the influence of *heat* some saturated hydrocarbons of the P. E. may be similarly decomposed by triphenylmethyl, to form the new substances with which the still undecomposed triphenylmethyl then combines. A complete working up of the reaction mixture has shown, however, that the by-products are not greater in amount than from any normal triphenylmethyl solution (about 15%), and no appreciable quantity of triphenylmethane was found among them. Consequently the new hydrocarbons could not have been formed at the expense of the triphenylmethyl. Second, triphenylmethyl may crystallize from the P. E. solution in combination with definite, saturated hydrocarbons therein present. Upon

¹ Lassar-Cohn, *Arbeits-Methoden* III Anflage p. 191.

heating these compounds to 90-110°, the reaction which produces the new hydrocarbons that distill off might take place, again at the expense of the triphenylmethyl. Peroxide determinations made upon the residue left after heating show, however, that it consists of almost pure triphenylmethyl. No reaction, therefore, takes place during the heating of the solid compounds involving the decomposition of triphenylmethyl. Third, there may be present in the P. E. some hitherto undescribed substances, not removed by the process of purification, which triphenylmethyl, under the influence of heat, singles out and with which it combines. On account of the difficulties of obtaining these volatile hydrocarbons in quantities large enough to work with, and the uncertain, complex nature of P. E., it is best to leave this question an open one, till the behavior of triphenylmethyl with saturated and unsaturated aliphatic and cyclic compounds can be further investigated.

8. BEHAVIOR OF TRIPHENYLMETHYL WITH CARBON DISULPHIDE AND CHLOROFORM.

A number of attempts were made to prepare compounds of triphenylmethyl with methyl, ethyl and isopropyl alcohols. On account of the extreme insolubility of triphenylmethyl in these alcohols, it was found necessary to employ, in addition, other solvents such as carbon disulphide and chloroform.

Experiment I. 5g. of triphenylmethyl were dissolved in 10cc. of chloroform and 17cc. of warm ethyl alcohol added. On cooling the solution an oil separated out which became crystalline on placing the apparatus in snow over night. These crystals, after washing with volatile petroleum ether and drying in vacuum, lost on heating to 110° 11.4% in weight. The liquid which distilled off during the heating was analyzed and was found to be about half chloroform.

Experiment II. Experiment I was repeated but the crystals were washed 7 times with absolute alcohol and then 4 times with volatile petroleum ether. After 1½ hours drying in vacuum they contained 6.7% of volatile liquid, which liquid was found to be 72% chloroform. 0.8117g. of the original substance was then finely powdered and dried for 1½ hours in a vacuum. The loss in weight was 0.3%. This same sample was then heated to 110° in a stream of carbon dioxide and lost 6.18%.

These experiments and others of similar nature show that the chloroform in the crystals cannot be merely mechanically occluded but must be present in some weak form of chemical combination which we are not in a position to define closer at present.

Experiment III. Experiment I was repeated using carbon disulphide instead of chloroform. On heating, 10.35% of volatile liquid was found in the crystals. The condensed liquid from the analysis had a high refractive index and the odor of carbon disulphide. Water shaken with it gave only a faint iodoform reaction, showing almost complete absence of ethyl alcohol.

Experiment IV. 6g. of triphenylmethyl were dissolved in 15cc. of freshly purified carbon disulphide. When the solution was cold 35cc. of cold purified petroleum ether were added. Crystals formed on leaving the apparatus in snow over night. 1.452g. of these crystals lost 0.5% on heating to 110° for one hour.

Experiment V. 8g. of triphenylmethyl were dissolved in carbon disulphide and treated as in V except that the apparatus stood at room temperature over night. (a) 4.587g. of the crystalline product lost at 110° , 0.456g. or 9.94%. (b) 0.341g. of the same product, finely powdered, lost 0.14% on drying for $2\frac{1}{2}$ hours in a vacuum. The liquid which distilled off in (a) was analyzed and found to be 75% carbon disulphide.

That triphenylmethyl under favorable conditions should combine with carbon disulphide is not surprising. The fact that sulphur changes its valence so readily from 2 to 4 would lead us to expect the formation of such addition compounds. A study of the behavior of triphenylmethyl toward mercaptans and other sulphur containing solvents will probably throw light on this question.

All of the addition compounds of triphenylmethyl which have been described in this paper give the characteristic reactions of triphenylmethyl. Their solutions in the presence of oxygen all give peroxide, and they will all add on iodine to form triphenylmethyl iodide. It is certain that in the solid state these compounds all contain combined solvent held much more firmly than is ever the case with so-called solvent of crystallization. In the case of the esters, ketones, and ether-compounds the combination is undoubtedly through the additional two valences of an oxygen atom just as in the oxonium salts, whose formation is assumed to be due to the tendency of oxygen to become tetravalent. In the oxonium salts too, the combination between the oxygen and the acid is so weak that solutions of the salts react as if all of the acid was present in the free state. In solutions of both the triphenylmethyl compounds and the oxonium salts there is then an equilibrium between the combined forms and the products of their dissociation, i. e., triphenylmethyl and ester, and acid and ester. If one of these products of dissociation, triphenylmethyl or the acid, is combined by the addition of some reagent then the dissociation will progress further till all of the triphenylmethyl or acid has been freed and used up. The manner in which the extra valences of oxygen are held by triphenylmethyl will be discussed further on in this paper. At the present time there seems to be no satisfactory hypothesis to explain the formation of the compounds of triphenylmethyl with hydrocarbons.

VI. EFFECT OF LIGHT UPON TRIPHENYLMETHYL.

In a previous paper¹ it has been pointed out that when 3% solutions

¹ Ber. d. chem. Ges. 37, 1641 (1904).

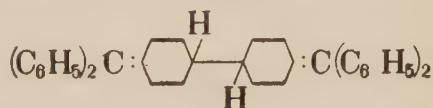
of the several analogues of triphenylmethyl, protected from air, are kept for some time the solutions gradually become decolorized and at the same time the substances lose their unsaturated character. We have now cleared up the cause of this peculiar change, and found it to be due to the effect of light upon these compounds. The analogues of triphenylmethyl are apparently more sensitive to the influence of light than the latter itself. While solutions of triphenylmethyl have been kept for longer than a year in diffused light with but slight decomposition, solutions of nearly all of its analogues lost their color under the same condition in about two months. The naphthyldiphenylmethyl compound alone, still retains considerable color after five months exposure. All of the earlier work upon triphenylmethyl was done in a poorly lighted room, so the effect of light was overlooked till the past spring, when, after a change to a lighter room, much trouble was experienced in obtaining pure triphenylmethyl. This difficulty has been found to be due to the presence of products formed by the action of light upon the hydrocarbon during the process of its preparation.

We find that a solution of triphenylmethyl in benzene, when exposed to direct sunlight rapidly decolorizes, the length of time necessary for complete decolorization depending upon the concentration of the solution as well as the thickness of the layer exposed. Three or four hours of bright sunlight will decolorize a 15% solution of triphenylmethyl in benzene when sealed in a specimen tube of 2 cm. internal diameter. In carbontetrachloride the reaction is more rapid, one hour being sufficient for decolorization, while in carbon disulphide the change is very slow, due probably to the cutting out of the actinic rays by the intense red color which the solution soon assumes. The total weight of products of the decomposition of triphenylmethyl in benzene solution by light, after all the benzene has been evaporated, is about 105% of the original triphenylmethyl taken. Of this the chief product is triphenylmethane, about 65%, while the rest consists of substances insoluble in ether, about 25%, and a strongly aromatic oil. The mixture insoluble in ether contains at least two substances, one melting at about 237°C. and the other at 194°C. These two bodies are very difficult to separate from each other as well as from traces of peroxide. The effect of direct sunlight upon triphenylmethyl in carbontetrachloride solution is very different from the above described effect in benzene. No triphenylmethane was found, but there was formed about 50% of an oil along with a mixture of crystalline substances which so far have not been identified. This difference of behavior in the absence of a hydrogen containing solvent, taken together with the increase in weight of total products during the reaction in benzene, indicates that the benzene enters into the reaction. That alcohols and ketones may, in the sunlight, act as reducing agents upon organic compounds dissolved in them, is

well known from the work of Ciamician and Silber.¹ Apparently also in the effect of light upon triphenylmethyl and its analogues the solvent benzene actually acts as a reducing agent. This behavior of triphenylmethyl toward light is somewhat analogous to that of tetraphenyl-p-xylylene recently described by Thiele,² and also partly to that of disubstituted butadiene dicarboxylic acid anhydrides observed by Stobbe.³ We may also mention in this connection that while Kahlbaum's triphenylmethane gives on exposure of its benzene solution to direct sunlight small amounts of an insoluble body, (probably para-anthracene), carefully purified triphenylmethane gave no trace of such product even after two months of exposure to direct sunlight.

VII. THE CONSTITUTION OF TRIPHENYLMETHYL.⁴

The hypothesis put forth by Prof. Gomberg in his first paper on triphenylmethyl, that this substance is best represented by the simple formula $(C_6H_5)_3C$, is in harmony with all of its chemical properties described in this and in previous papers. Now, however, since the molecular weight of the substance has been shown to be twice that which would be required by this simple hypothesis several suggestions of structures that would be in harmony with this new fact have been made: (1) Heintschel⁵ has suggested a quinoid structure which would make triphenylmethyl appear as a derivative of diphenyl;



(2) Tschitschibabin,⁶ Hantzsch,⁷ and others have thought that triphenylmethyl might be in reality hexaphenylethane; (3) Jacobson⁸ has suggested a quinol like structure,



and (4), Gomberg and Cone⁹ have thought that triphenylmethyl should

¹ Ber. d. chem. Ges. 34, 1532 (1901).

² Ber. d. chem. Ges. 37, 1465 (1904).

³ Ber. d. chem. Ges. 37, 2237 (1904).

⁴ In order to make this discussion of any value references to the literature up to June, 1907, have been included, although the actual experimental work included in this thesis was finished by June, 1905.

⁵ Ber. d. chem. Ges. 36, 320, 409 (1903).

⁶ Ibid. 40, 367, (1907).

⁷ Ibid. 39, 2478 (1906).

⁸ Ibid. 38, 196 (1905).

⁹ Ibid. 38, 2453 (1905).

be still represented by the simple formula $(C_6H_5)_3C$, but that in solution it exists associated into a dimolecular complex exactly as do a great many other substances as e. g. acetic acid.

(1) The suggestion of Heintschel is entirely inadequate for the reason that it is contrary to experience to assume that a diphenyl derivative would so readily break the linking between the two phenyl groups. Willstätter's¹ recent work on diphenoquinone, which was found to be very stable, fully confirms this view.

(2) The arguments that have been put forth in favor of considering triphenylmethyl as identical with hexaphenylethane are two in number: First, triphenylmethyl has in solution the same molecular weight that hexaphenylethane would have. Second, pentaphenylethane as compared with tetraphenylethane is easily decomposed and it may therefore be concluded that hexaphenylethane would be still more unstable, even perhaps as unstable as triphenylmethyl itself. These arguments make no distinction between triphenylmethyl in solution and in the solid state. In solution triphenylmethyl is intensely colored while in the solid state it is colorless and it cannot, therefore, be represented by the same formula in both conditions. In solution triphenylmethyl cannot be hexaphenylethane, as will be shown conclusively in the next paragraph. As to what is the structure of triphenylmethyl in the solid state, at present the facts known do not warrant saying definitely, it may be either hexaphenylethane or it may be the free radicle $(C_6H_5)_3C$.

(3 and 4) At the time that the suggestion of the quinol like structure was made by Jacobson there was nothing to support such an assumption beyond the molecular weight of triphenylmethyl. Gomberg and Cone considered that all of the chemical reactions of triphenylmethyl could be explained better by their simple assumption of association of triphenylmethyl into a dimolecular form. This assumption would also be in harmony with the results of the molecular weight determinations. Since this suggestion of association was made by Gomberg and Cone they have tested the validity of the quinol formula of Jacobson by studying the action of metals upon halogen substituted triphenylmethylchlorides.² If a tri-p-halogen substituted triphenylmethylchloride is treated with molecular silver it should form an unsaturated body entirely analogous to triphenylmethyl. This unsaturated compound should have a halogen atom in the place of the quinol hydrogen atom in the simple triphenylmethyl, attached to the carbon atom marked with the star (*) in the above formula of Jacobson's. Such a halogen atom should be labile and it should be possible to remove it by shaking this compound further with molecular silver. If Jacobson's formula represents the true state of affairs in triphenylmethyl, then, when a p-halogen derivative of triphenylmethylchloride

¹ Ber. d. chem. Ges. 38, 1234 (1905).

² Ber. d. chem. Ges. 39, 3274 (1906).

is shaken with molecular silver nucleus halogen should be removed as well as carbinol halogen. This is exactly what does take place, as has been shown in a large number of cases by Gomberg and Cone,¹ and by Gomberg.² Jacobson's formula appears so far then to be the best suggestion that has been made for the structure of triphenylmethyl.

The fact that triphenylmethyl when dissolved in liquid sulphur dioxide is a good conductor of electricity indicates that it undergoes some sort of dissociation. If it is best represented by Jacobson's formula then it would probably dissociate into a quinoid ion $(\text{C}_6\text{H}_5)_2\text{C}=\text{C}_6\text{H}_4\text{--}^\text{H}$ and a benzoid ion $(\text{C}_6\text{H}_5)_3\text{C}$. In the presence of reagents which would combine with either one of these ions the dissociation would progress as fast as the ion was removed until finally all of the triphenylmethyl would be used up. This explanation assumes that the benzoid and the quinoid ions are tautomeric forms and are changeable one into the other according to the conditions of equilibrium. Viewed in this light it is apparent why triphenylmethyl, even though it is best represented by Jacobson's formula, reacts in all cases as if it were the free radical $(\text{C}_6\text{H}_5)_3\text{C}$. If to a solution of triphenylmethyl an oxygen containing solvent, as an ester or a ketone, is added the extra two valences of the oxygen will take up triphenylmethyl radicles to form a compound of the type,



which is more insoluble than triphenylmethyl itself. As the solution cools this compound crystallizes out in preference to the triphenylmethyl itself and so the equilibrium in the solution is disturbed. More triphenylmethyl then dissociates and combines with the oxygen containing solvent and this in turn crystallizes out. This process continues till all of the triphenylmethyl has been changed over into the compound with the solvent.

The study of triphenylmethyl and its analogues is still being continued in this laboratory and it is hoped that in the near future enough will be known of this class of substances so that a satisfactory explanation of the compounds of triphenylmethyl with hydrocarbons and other solvents can be also given.

¹ Loc. cit.

² *Ibid.* 40, 1847 (1907).

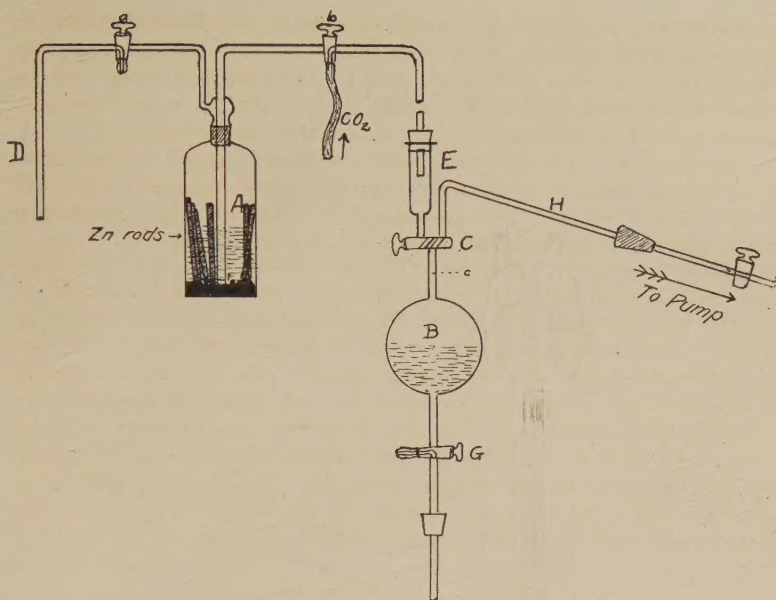


PLATE I

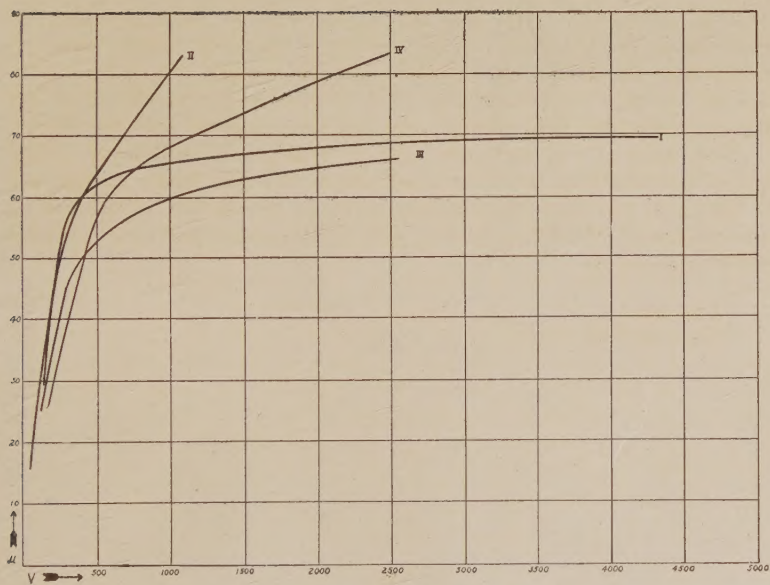


PLATE II

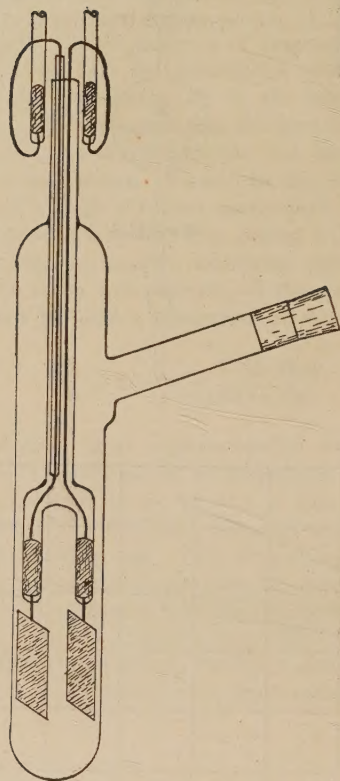


PLATE III

